

PATENT SPECIFICATION

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(54) POLYESTER POLYOLS SUITABLE FOR USE IN THE MANUFACTURE OF RIGID POLYURETHANE FOAMS

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the manufacture of a rigid polyurethane foam from an organic polyisocyanate and relatively high molecular weight polyhydroxy compounds, and to polyester-ols for use therein.

A review of the manufacture and properties of rigid polyurethane foams is to be found, for example, in *Kunststoff-Handbuch*, Volume VII "Polyurethane" by R. Vieweg and A. Höchtlen, pages 504 et seq. (published by Carl Hanser, Munich 1966).

The conventional method of manufacturing rigid polyurethane foams is to react relatively high molecular weight polyhydroxy compounds, preferably polyether-ols or polyester-ols, with aromatic polyisocyanates, especially toluylene diisocyanates and mixtures of diphenylmethane diisocyanates and polyphenyl-polymethylene polyisocyanates in the presence of water or of compounds which split off water, and of blowing agents, emulsifiers, catalysts and other assistants and additives, using the one shot, prepolymer or semi-prepolymer method. It has also been proposed to use, in place of polyether-ols or polyester-ols, mixtures of the said components for the manufacture of the rigid foams. One factor leading to this latter method is cost reduction, achieved by mixing expensive polyester-ols, suitable for the manufacture of high quality rigid polyurethane foams, with cheaper polyether-ols. Up to the present time, the polyester-ol employed is in the main a product of phthalic acid, adipic acid, oleic acid and trimethylolpropane, which has a hydroxyl number of 380. A particular disadvantage of this polyester-ol, apart from its high price, is its high viscosity, which can present processing difficulties.

These processing difficulties manifest themselves particularly in polyurethane systems which are used by the two-component method, the A component conventionally consisting of relatively high molecular weight polyhydroxy compounds, chain extenders, blowing agents, catalysts, auxiliaries and additives, and the B component of organic polyisocyanates. To achieve good processability and a high quality of rigid polyurethane foam it is essential that the A component should have a viscosity of less than 1,000 cp.

Netherlands Laid-Open Application 7,500,964 discloses that polyester-ols which are obtained by condensing one or more polyols with a mixture of aliphatic dicarboxylic acids containing from 5 to 95% by weight of glutaric acid, may be used for the manufacture of polyurethanes. Mixtures of glutaric acid, adipic acid and succinic acid are cited as mixtures of aliphatic dicarboxylic acids. The polyester-ols described are in particular used for the manufacture of micro-cellular elastomers, for example for shoe soles; to manufacture such elastomers, the reactive mixture of polyester-ol, butanediol, water, amine catalyst and 4,4'-diphenylmethane diisocyanate is allowed to foam in a closed mold, the volume of which is about half the volume which the product would occupy on free foaming.

Suitable cheap polyester-ols, having a low viscosity, for the manufacture of high quality rigid polyurethane foams have not previously been disclosed.

The present invention seeks to provide cheap polyester-ols of low viscosity, which can be used for the manufacture of high quality rigid polyurethane foams and which can in particular be processed, without problems, by the two-component method, the A component having a viscosity of less than 1,000 cp at 23°C.

Accordingly, the present invention relates to a process for the manufacture of a rigid polyurethane foam which includes reacting an organic polyisocyanate and polyhydroxy compounds in the presence of a catalyst, with or without a chain extender, a blowing agent and/or one or more assistants and additives, wherein the polyhydroxy compounds used are a mixture of a polyether-ol and a polyester-ol, the polyester-ol being obtained by condensing a dicarboxylic acid mixture which contains from 20 to 35% by weight of succinic acid, from 35 to 50% by weight of glutaric acid and from 20 to 32% by weight of adipic acid, based on the total weight of the said dicarboxylic acids, with an isopropanolamine mixture and/or hexanetriol isomer mixture, with or without one or more other low molecular weight polyols having a molecular weight up to 300.

For the purposes of the present invention, particularly suitable isopropanolamine mixtures are those which contain from 5 to 40% by weight, preferably from 15 to 25% by weight, of diisopropanolamine and from 95 to 60% by weight, preferably from 85 to 75% by weight, of triisopropanolamine, based on the total weight of diisopropanolamine and triisopropanolamine, which isopropanolamine mixture may in addition contain up to at most 8% by weight, preferably up to 3% by weight, based on total weight, of by-products. The isopropanolamine mixtures contain hydrogen atoms, capable of reacting with phthalic anhydride, which generally correspond to an OH number of from 830 to 950, preferably from 860 to 920 (mg of KOH/g).

Appropriate isopropanolamine mixtures can be obtained, for example, as by-products from the manufacture of diisopropanolamine from ammonia or isopropanolamine and propylene oxide.

For the purposes of the invention, particularly suitable hexanetriol isomer mixtures are mixtures which contain from 40% by weight to 99.8% by weight, preferably from 50 to 99% by weight, based on the total weight of the isomer mixture, of 2,4-dihydroxy-3-methylolpentane, with or without other hexanetriol isomers, eg. 1,3,5-trihydroxy-hexane, and small amounts of diols. The products have an iodine color number which in general should not exceed 10, preferably of from 6 to 8, an OH number generally of from 890 to 1,250, a refractive index generally of from 1.468 to 1.470 at 20°C and a density generally of from 1.05 to 1.07 g/ml at 20°C. Appropriate hexanetriol isomer mixtures are obtained, for example, as by-products of the manufacture of butane-1,3-diol from acetaldehyde by an aldol condensation.

The isopropanolamine mixtures and hexanetriol isomer mixtures may be used separately or mixed with one another, and in the latter case the ratio of isopropanolamine mixture to hexanetriol isomer mixture may be varied within wide limits, for example within weight ratios of from 10 : 1 to 1 : 10, preferably from 2 : 1 to 1 : 2.

To manufacture special rigid polyurethane foams it has furthermore proved advantageous to use polyester-ols obtained by a condensation in which the above isopropanolamine mixtures and/or hexanetriol isomer mixtures are replaced partially, for example to the extent of up to 75 mole per cent, preferably up to 50 mole per cent, by an equimolar amount of a low molecular weight polyol, which polyol is present as co-condensed units in the resulting polyester-ol. Suitable low-molecular weight polyols are especially those with molecular weights of from 62 to 300, preferably from 62 to 200, which contain from 2 to 4 hydroxyl groups in the molecule. Specific examples are glycols, eg. butane-1,4-diol, hexane-1,6-diol, decane-1,10-diol, diethylene glycol, dipropylene glycol and, preferably, ethylene glycol and propylene glycol, triols, eg. glycerol and trimethylolpropane, and pentaerythritol.

The other starting component for the manufacture of the polyester-ols is a dicarboxylic acid mixture which comprises from 20 to 35% by weight, preferably from 28 to 33% by weight, of succinic acid, from 35 to 50% by weight, preferably from 40 to 45% by weight, of

glutaric acid and from 20 to 32% by weight, preferably from 24 to 28% by weight, of adipic acid, based on the total weight of the said dicarboxylic acids. In addition, the dicarboxylic acid mixture may contain up to 5% by weight, preferably from 2 to 3% by weight, based on total weight, of impurities which essentially consists of imides of succinic acid and of glutaric acid. Dicarboxylic acid mixtures of the said type can be obtained, for example, as by-products of the manufacture of adipic acid by oxidizing cyclohexanol or cyclohexanone with nitric acid.

In order to manufacture rigid polyurethane foams having special properties, it may be necessary to modify the polyester-ols by the inclusion of radicals which increase the hardness of the product, and/or of unsaturated groups. In such cases it has proved advantageous to employ, in addition to the aliphatic dicarboxylic acid mixture, other, preferably aromatic and/or ethylenically unsaturated, dicarboxylic acids and/or their esterifiable derivatives, in amounts of from 5 to 50 mole per cent, preferably from 10 to 30 mole per cent, based on the total amount of dicarboxylic acids employed, for the manufacture of the polyester-ols by condensation. Specific examples of dicarboxylic acids and dicarboxylic acid derivatives of the above type are phthalic acid, phthalic anhydride, terephthalic acid, dimethyl terephthalate, bis-2-hydroxyethyl terephthalate, maleic acid, maleic anhydride and fumaric acid.

The polyester-ols which are to be used for the manufacture of rigid polyurethane foams can be obtained by conventional methods, for example by condensation under azeotropic conditions or, preferably, by melt condensation, in the presence or absence of conventional and common esterification catalysts. For this purpose, the aliphatic dicarboxylic acid mixture is reacted with the isopropanolamine mixture and/or hexanetriol isomer mixture, with or without other dicarboxylic acids and low-molecular weight polyols, in such amounts that the ratio of carboxyl groups to hydroxyl groups in the components from which the polyester is formed is generally from 1 : 1.5 to 1 : 3.5, preferably from 1 : 1.75 to 1 : 3. Instead of the aliphatic dicarboxylic acid mixture, ester-forming derivatives of these dicarboxylic acids, for example mixtures of anhydrides or of monoalkyl esters and/or dialkyl esters where alkyl is of 1 to 5 carbon atoms, preferably dimethyl esters, of these dicarboxylic acids may also be employed. The polycondensation is generally carried out at a reaction temperature of from 100 to 250°C, preferably from 130 to 220°C, under atmospheric or reduced pressure. Generally, the polyester-ols used have hydroxyl numbers of from 180 to 650, preferably from 250 to 450, acid numbers less than 3, preferably from 0.3 to 2, and functionalities of from 2.5 to 6, preferably from 3.0 to 4.5. The products generally have viscosities, at 75°C, of from 50 to 1,000 mPas, preferably from 50 to 700 mPas.

To manufacture the rigid polyurethane foams relatively high-molecular weight polyhydroxy compounds, organic polyisocyanates and catalysts, with or without chain extenders, blowing agents, assistants and additives, are used, as already mentioned.

The relatively high-molecular weight polyhydroxy compounds comprise mixtures of the above polyester-ols with conventional polyether-ols.

The polyether-ols suitably have molecular weights of from about 200 to about 6,500, preferably from about 250 to about 1,000, and hydroxyl numbers of from 25 to 800, preferably from 250 to 500, and may be manufactured by reacting one or more alkylene oxides, which may or may not be substituted and where alkylene is of 2 to 4 carbon atoms, with a starter molecule which contains at least two active hydrogen atoms in the molecule. Examples of alkylene oxides are 1,2- and 2,3-butylene oxide, styrene oxide, epichlorohydrin, tetrahydrofuran and, preferably, ethylene oxide and propylene oxide. The alkylene oxides may be used individually, in alternating succession, or as mixtures.

Examples of suitable starter molecules are water; phosphoric acid; ammonia; hydrazines and aliphatic, cycloaliphatic and aromatic amines, eg. ethylenediamine, N,N'-dimethylethylenediamine, tetramethylenediamine, hexamethylenediamine, diethylenetriamine, o-, m- and p-phenylenediamine, 2,4- and 2,6-diaminotoluene, 1,4-, 1,5- and 1,8-naphthylene-diamine, 2,4'-, 2,2'-, 4,4'-diaminodiphenylmethane and melamine; amino alcohols, eg. ethanolamine, diethanolamine and triethanolamine; polycarboxylic acids, eg. adipic acid and terephthalic acid; and, preferably, polyhydroxy compounds and polyphenols, eg. ethylene glycol, diethylene glycol, polyethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, butane-2,4-diol, hexane-1,6-diol, but-2-yne-1,4-diol, but-2-ene-1,4-diol, glycerol, trimethylolpropane, hexane-2,4,6-triol, pentaerythritol, sorbitol, sucrose, resorcinol, hydroquinone, 3-hydroxy-2-naphthol, 6,7-dihydroxy-1-naphthol, 2,2-bis-(p-hydroxyphenyl)-propane, 4,4'-dihydroxydiphenylmethane and 1,1,2-tris-(p-hydroxyphenyl)-ethane.

The polyester-ols and polyether-ols are suitably used in such amounts that the mixture contains from 1 to 70% by weight, preferably from 20 to 50% by weight, of polyester-ols

and from 99 to 30% by weight, preferably from 80 to 50% by weight, of polyether-ols, based on the total weight of the polyester-ol/polyether-ol mixture.

Suitable isocyanates for the manufacture of the rigid polyurethane foams are organic polyisocyanates of the formula $R(NCO)_n$, where R is a polyvalent, aliphatic, cycloaliphatic, alkylaromatic or aromatic organic radical or a mixed radical of this type and n is an integer which corresponds to the valency of R and is at least two. Examples of typical organic polyisocyanates to be used for the purposes of the invention are aromatic polyisocyanates, eg. 2,4- and 2,6-toluylene diisocyanate, 2,2'-, 2,4'- and 4,4'-diphenylmethane diisocyanate, triphenylmethane triisocyanates, biphenyl diisocyanates, m- and p-phenylene diisocyanate and 1,5-naphthylene diisocyanate and cycloaliphatic and aliphatic polyisocyanates, eg. isophorone diisocyanate and hexamethylene diisocyanate. The use of crude and pure toluylene diisocyanates and of mixtures of 2,2'-, 2,4'- and 4,4'-diphenylmethane diisocyanate and polyphenyl-polymethylene polyisocyanates is preferred. The polyisocyanates may be used individually or as mixtures.

Conventional catalysts, for example tertiary amines, eg. dimethylbenzylamine, dicyclohexylmethylamine, dimethylcyclohexylamine, N-methyl- and N-ethyl-morpholine, dimethyl-piperazine, pyridine, 1-aza-bicyclo-(3,3,0)-octane, dimethylaminoethanol, 1,2-dimethylimidazole and preferably triethylenediamine, and metal salts, eg. iron-II chloride, zinc chloride and preferably tin-II salts and dibutyl-tin dilaurate, are added to the reaction mixture in order to accelerate the reaction of the relatively high molecular weight polyhydroxy compounds, with or without chain extenders and water, with the organic polyisocyanates. To achieve advantageous reaction times from the point of view of foaming, the amount of catalyst to be employed is determined empirically in accordance with the reactivity of the particular catalyst or catalyst mixture.

It may or may not be advantageous to employ chain extenders, additionally to the relatively high molecular weight polyhydroxy compounds, in the process according to the invention for the manufacture of rigid polyurethane foams. The chain extenders generally have molecular weights of less than 2,000, preferably of from 30 to 600, and preferably contain two active hydrogen atoms. Examples of suitable chain extenders are aliphatic and/or aromatic diols of 2 to 14, preferably of 4 to 10, carbon atoms, eg. ethylene glycol, propanediol, decane-1,10-diol and preferably butane-1,4-diol, hexane-1,6-diol and bis-(2-hydroxyethyl)-hydroquinone, diamines, eg. ethylenediamine and 4,4'-diaminodiphenylmethane, ethanolamines, eg. triethanolamine, and polyhydroxy compounds, eg. glycerol, trimethylolpropane and low-molecular weight hydroxyl-containing polyalkylene oxides.

Blowing agents which may or may not be used in carrying out the process according to the invention include water, which reacts with isocyanate groups to form carbon dioxide. The amounts of water which may advantageously be used are from 0.1 to 2%, based on the weight of polyol. Larger amounts of water may also be used but it is preferred not to do so if the heat stability or heat insulation properties are particularly important.

Other suitable blowing agents which may be used preferably are low-boiling liquids which vaporize under the influence of the exothermic polymerization reaction. Liquids which are inert towards the organic polyisocyanate and have boiling points not exceeding 100°C under atmospheric pressure, preferably boiling points of from -40 to +50°C, are suitable. Examples of preferred liquids of this type are halohydrocarbons, eg. methylene chloride, trichlorofluoromethane, dichlorodifluoromethane, dichloromonofluoromethane, dichlorotetrafluoroethane and 1,1,2-trichloro-1,2,2-trifluoroethane. Mixtures of these low-boiling liquids with one another and/or with other substituted or unsubstituted hydrocarbons may also be used.

The most appropriate amount of low-boiling liquid to be used for the manufacture of rigid foams depends on the density of the foam to be obtained and on whether water is or is not used at the same time. In general, amounts of from 5 to 40 per cent by weight, based on organic polyisocyanate, give satisfactory results.

Assistants and additives may also be incorporated into the reaction mixture. Examples include stabilizers, hydrolysis inhibitors, pore regulators, fungistatic and bacteriostatic materials, dyes, pigments, fillers, surfactants, plasticizers and flameproofing agents.

For example, it is possible to use surfactants which serve to assist the homogenizing of the starting materials and may also serve to regulate the cell structure of the foams. Examples include siloxane-oxyalkylene copolymers and other organopolysiloxanes, oxyethylated alkylphenols, oxyethylated fatty alcohols, paraffin oils, castor oil esters and ricinoleic acid esters and turkey red oil; these are employed in amounts of from 0.2 to 6 parts by weight per 100 parts by weight of polyisocyanate.

It may also be advantageous to introduce a plasticizer into the reaction mixture to reduce the brittleness tendency of the products. Conventional plasticizers may be used, but it is particularly advantageous to employ plasticizers which contain phosphorus and/or halogen

atoms and hence additionally improve the fire resistance of the polyurethane plastics. Such plasticizers include tricresyl phosphate, tris-2-chloroethyl phosphate, tris-chloropropyl phosphate and tris-2,3-dibromopropyl phosphate.

In addition to the above halogen-substituted phosphates, inorganic flameproofing agents, eg. antimony trioxide, arsenic oxide, ammonium phosphate and calcium sulfate may also be used to fireproof the polyurethane foams. In general it has proved advantageous to use from 5 to 50 parts by weight, preferably from 5 to 25 parts by weight, of the said flameproofing agents per 100 parts by weight of organic polyisocyanate.

The rigid polyurethane foams are suitably manufactured by the prepolymer method and preferably by the one shot method. For this purpose, the relatively high molecular weight polyhydroxy compounds, with or without chain extenders, and the organic polyisocyanates are reacted generally at from 10 to 60°C, preferably from 18 to 40°C, in such ratios as to provide, in the reaction mixture, generally from 1 to 1.2, preferably from 1.05 to 1.15, NCO groups of the polyisocyanate per hydroxyl group from the relatively high molecular weight polyhydroxy compounds with or without chain extenders. If a mixing chamber with several feed nozzles is used, the polyisocyanate, the relatively high molecular weight polyhydroxy compounds, the catalyst and, where these are used, the chain extenders, blowing agents, assistants and additives may be introduced as individual materials and mixed thoroughly in the mixing chamber. However, it has proved particularly advantageous to use the two-component method and combine the mixture of polyether-ols and polyester-ols with the catalyst, the blowing agent, the assistants and the additives to form component A, whilst using the organic polyisocyanates as component B. Advantages of this method are that the components A and B can be stored separately for a certain period and need only be mixed thoroughly before manufacturing the rigid polyurethane foam, and, especially, that component A has a viscosity of less than 1,000 cp, preferably of from 200 to 800 cp, and can therefore be processed easily.

The rigid polyurethane foams manufactured by the process according to the invention generally have densities of from 25 to 300 kg/m³, preferably from 30 to 100 kg/m³, and are distinguished by a fine cell structure, dimensional stability and a high level of mechanical properties, especially a high compressive strength. The products are preferably used as insulating materials.

In the Examples, parts are by weight.

EXAMPLE 1

Manufacture of the polyester-ols

534 parts of a dicarboxylic acid mixture comprising 29 parts of succinic acid, 44 parts of glutaric acid, 26 parts of adipic acid and 1 part of impurities per 100 parts of mixture, 248 parts of ethylene glycol and 754 parts of an isopropanolamine mixture containing 80% by weight of triisopropanolamine, based on the total weight of diisopropanolamine and triisopropanolamine, are mixed and condensed under nitrogen, whilst steadily raising the temperature up to a bottom temperature of 200°C, until no further water of condensation is eliminated. Condensation is then continued at 210°C under reduced pressure (down to 100 mm Hg) until the acid number of the reaction mixture is less than 3. The excess ethylene glycol is then distilled off, and the hydroxyl number of the polyester-ol adjusted, at a bottom temperature of 200°C under reduced pressure (down to 50 mm Hg). The total condensation time is about 11 hours. 267 parts of distillate are removed. The polyester-ol obtained has a hydroxyl number of 331, an acid number of 0.5 and a viscosity of 440 mPas at 75°C.

EXAMPLES 2 to 7

If the procedure described in Example 1 is followed but the starting components are varied, the polyester-ols having the characteristics shown in Table 1 are obtained.

The hexanetriol isomer mixture used for the manufacture of the polyester-ols had an OH number of 902.

TABLE 1
Characteristics of polyester-ols obtained in Examples 2 to 7

Ex- ample	Starting materials	Parts	Amount of distillate parts	Condensation time [h]	Hydroxyl number mg of KOH/g	Acid number mg of KOH/g	Viscosity mPas, 75°C
2	Dicarboxylic acid mixture as described in Example 1 ethylene glycol isopropanolamine mixture as described in Example 1	534 310 566	264	5	310	1.4	340
3	dicarboxylic acid mixture as described in Example 1 propylene glycol isopropanolamine mixture as described in Example 1	534 304 754	298	6	311	1.3	720
4	dicarboxylic acid mixture as described in Example 1 propylene glycol isopropanolamine mixture as described in Example 1	534 380 566	292	7	299	1.5	410
5	dicarboxylic acid mixture as described in Example 1 ethylene glycol hexanetriol isomer mixture	1,500 698 1,926	798	19	335	0.9	170

TABLE 1 (continuation)
Characteristics of polyester-ols obtained in Examples 2 to 7

Ex- ample	Starting materials	Parts	Amount of distillate parts	Condensation time [h]	Hydroxyl number mg of KOH/g	Acid number mg of KOH/g	Viscosity mPas, 75°C
6	dicarboxylic acid mixture as described in Example 1 isopropanolamine mixture as described in Example 1	400 1,131	129	8	378	1.5	680
7	dicarboxylic acid mixture as described in Example 1 phthalic anhydride ethylene glycol hexanetriol isomer mixture	534 592 538 1,430	531	23	332	1.0	300

EXAMPLES 8 TO 14

Manufacture of the rigid polyurethane foams

General manufacturing instructions

- 5 Component A: 5
- 36.99 parts of a commercial polyether-ol based on ethylenediamine (as the starter) and propylene oxide, and having a hydroxyl number of 460 - 500
- 36.99 parts of polyester-ol
- 10 0.69 part of a silicone-based foam stabilizer (DC 190, a commercial product from Dow Corning) 10
- 0.57 part of amine catalyst (Desmorapid PP from Bayer, "Desmorapid" is a Registered Trade Mark)
- 0.9 part of water
- 0.9 part of ethoxylated castor oil
- 15 22.95 parts of trichlorofluoromethane 15
- Component B:
- A mixture of diphenylmethane diisocyanates and polyphenyl-polymethylene polyisocyanates (crude MDI).
- 20 To manufacture the rigid polyurethane foams, components A and B are mixed in the weight ratio of 1 : 1.1. To determine the start time and rise time, 420 g of the foamable mixture are allowed to foam freely in a rectangular mold having a base area of 20 × 20 cm. The resulting fine-celled rigid polyurethane foam blocks are used to determine the compressive strength by the method of DIN 53,421 and the flexural strength and deflection
- 25 by the method of DIN 53,423. 25
- The polyester-ols used to manufacture the rigid polyurethane foams, the start times and rise times found, and the mechanical properties of the products, are summarized in Table 2.

TABLE 2

Composition of the polyester-ols used for the manufacture of the rigid polyurethane foams, start times and rise times found, and mechanical properties of the end products

Examples	Polyester-ol	Start time [sec]	Rise time [sec]	Density [g/l]	Flexural strength [kp/cm ²]	Deflection [mm]	Compressive strength [kp/cm ²]
8	prepared as described in Example 1	12	95	28.7	2.97	15.1	2.31
9	prepared as described in Example 2	13	105	28.2	3.08	14.9	2.31
10	prepared as described in Example 3	15	125	28.5	3.31	14.1	2.38
11	prepared as described in Example 4	14	113	27.9	3.05	13.8	2.34
12	prepared as described in Example 5	19	88	27.4	3.2	16.4	2.1
13	prepared as described in Example 6	15	107	28.8	3.38	11.1	2.31
14	prepared as described in Example 7	15	103	27.1	3.0	13.9	2.2
Comparative Examples							
A	commercial product based on phthalic acid, adipic acid, oleic acid and trimethylolpropane; hydroxyl number 380	10	88	27.2	2.95	12.8	2.06
B	"	20	100	28.6	3.3	10.9	2.2
C	"	18	112	27.4	2.6	11.4	1.8

Viscosity of component A

Using various polyester-ols, component A was found to have the following viscosities at 23°C.

5	Polyester-ol	Viscosity, mPas at 23°C	5
	prepared as described in Example 1	690	
10	prepared as described in Example 5	540	10
	commercial product based on phthalic acid, adipic acid, oleic acid and trimethylolpropane	1,500	

15 WHAT WE CLAIM IS:-

1. A process for the manufacture of a rigid polyurethane foam which includes reacting an organic polyisocyanate and polyhydroxy compounds in the presence of a catalyst, with or without a chain extender, a blowing agent and/or one or more assistants and additives, wherein the polyhydroxy compounds used are a polyether-ol/polyester-ol mixture, the polyester-ol being obtained by condensing a dicarboxylic acid mixture which contains from 20 to 35% by weight of succinic acid, from 35 to 50% by weight of glutaric acid and from 20 to 32% by weight of adipic acid, based on the total weight of the said dicarboxylic acids, with an isopropanolamine mixture and/or hexanetriol isomer mixture, with or without one or more other polyols having a molecular weight up to 300.

2. A process as claimed in claim 1, wherein the polyester-ol/polyether-ol mixture contains from 1 to 70% by weight of polyester-ol and from 99 to 30% by weight of polyether-ol, based on the total weight of the polyester-ol/polyether-ol mixture.

3. A process as claimed in claim 1 or 2, wherein an isopropanolamine mixture which contains from 5 to 40% by weight of diisopropanolamine and from 95 to 60% by weight of triisopropanolamine, based on the total weight of diisopropanolamine and triisopropanolamine, is used to obtain the polyester-ol.

4. A process as claimed in claim 1 or 2, wherein a hexanetriol isomer mixture which contains from 40 to 99% by weight of 2,4-dihydroxy-3-methylolpentane, based on the total weight of the isomer mixture, is used to obtain the polyester-ol.

5. A process as claimed in claim 1 or 2, wherein an isopropanolamine mixture as defined in claim 3 and a hexanetriol isomer mixture as defined in claim 4 are used in a weight ratio of from 1 : 10 to 10 : 1 to obtain the polyester-ol.

6. A process as claimed in any of claims 1 to 5, wherein the polyester-ol is obtained from an isopropanolamine mixture and/or a hexanetriol mixture and in addition up to 75 mole per cent of a polyol having a molecular weight of from 62 to 300 and containing from 2 to 4 hydroxyl groups in the molecule, the mole per cent being based on the total moles of polyol, isopropanolamine and/or hexanetriol isomer.

7. A process as claimed in any of claims 1 to 6, wherein the polyester-ol is obtained from an acid mixture of from 28 to 33% by weight of succinic acid, from 40 to 45% by weight of glutaric acid and from 24 to 28% by weight of adipic acid, based on the total weight of the said dicarboxylic acids.

8. A process as claimed in any of claims 1 to 7, wherein from 10 to 30 mole per cent of the acid component from which the polyester-ol is obtained is an aromatic or ethylenically unsaturated dicarboxylic acid.

9. A process as claimed in any of claims 1 to 8, wherein the polyester-ol has a hydroxyl number of from 180 to 650, an acid number of less than 3, a functionality of from 2.5 to 6 and a viscosity at 75°C of from 50 to 1,000 m.Pas, and the polyether-ol has a molecular weight of from 200 to 6,500 and a hydroxyl number of from 25 to 800.

10. A process as claimed in any of claims 2 to 9, wherein the polyester-ol/polyether-ol mixture contains from 20 to 50% by weight of polyester-ol and from 80 to 50% by weight of polyether-ol based on the total weight of the polyester-ol/polyether-ol mixture.

11. A process as claimed in any of claims 1 to 10, wherein a polyester-ol is used which has been obtained by a process carried out substantially as described in any of the foregoing Examples 1 to 7.

12. A process for the manufacture of a rigid polyurethane foam carried out substantially as described in any of the foregoing Examples 8 to 14.

13. Rigid polyurethane foams when manufactured by a process as claimed in any of claims 1 to 12.

14. A polyester-ol obtained as defined in any of claims 1, 3 to 8 or 11.

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